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HIGH TEMPERATURE CERAMIC SUPERCONDUCTORS

FOR PERIOD
APRIL 1, 1991 – JUNE 30, 1991

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APPROVED FOR PUBLIC RELEASE

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DIRECTOR, DEFENSE MATERIALS

GENERAL ATOMICS PROJECT 3850
JUNE 1991

GENERAL ATOMICS

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1. INTRODUCTION

This is the eighth and final quarterly progress report on the work performed in the period from April 1, 1991 to June 30, 1991, on Office of Naval Research (ONR) Contract N00014-88-C-0714, entitled "High-Temperature Ceramic Superconductors." The principal objectives of this program are (1) to demonstrate fabrication of high-temperature ceramic superconductors that can operate at or above 90 K with appropriate current density, J_c, in forms useful for application in resonant cavities, magnets, motors, sensors, computers, and other devices; and (2) to fabricate and demonstrate selected components made of these materials, including microwave cavities and magnetic shields.

1.1. PROJECT OUTLINE

This program consists of six tasks: (1) metal alkoxide synthesis and processing, (2) microstructural evaluation and property measurement, (3) electrical and magnetic property measurement, (4) superconductor ceramic processing, (5) component fabrication and demonstration, and (6) reporting.

Task 1 is to synthesize a homogeneous alkoxide solution that contains all the constituent elements that can be easily made into powders, thin film, or drawn into fiber form. Ideally, this solution should possess precise stoichiometry, adequate stability, polymerizability, adherence, and spinnability. Also, the polymeric materials formed from this solution should be thermosetting, be able to be dissolved in organic solvents, and contain as little as possible low-temperature pyrolyzable organics with high char yield.

Task 2 is to study the microstructure as a function of processing parameters. The study includes: density, pore size and pore size distribution, phase identification, chemical composition and purity, environmental stability, effects of heat treatment, residual strain, seeding, annealing in magnetic fields, and epitaxy on grain growth and orientation.

Task 3 is to study the electrical and magnetic properties of the $YBa_2Cu_3O_7$ (123) high T_c ceramic superconductors. It will include both the ac electrical resistance (R_{ax}) and the ac magnetic susceptibility (χ_{ac}).

Task 4 is to investigate superconductor ceramic processing. Most of the important applications of superconductors require material in the form of fiber or films. Magnets, conductors, motors, and generators are examples of applications employing fiber; while detectors, microwave cavities, and microcircuitry require superconducting material in the form of films. The sol-gel process is ideally suited to producing materials in these forms; in fact, it is used commercially to produce anti-reflection and mirror coatings and to produce continuous ceramic fibers for structural reinforcement in composite materials and for thermal insulation.

Originally Task 5 was to demonstrate component fabrication. GA under the original SWO had to design and build a high Q, high T_c superconduction cavity using it unique sol-gel coating process capabilities. This task would have proceeded after some initial coating tests verified dc superconductivity and questions of adhesiveness, surface preparation, and processing procedures were answered. As the fabrication process and the materials quality were improved throughout the three-year program, two additional cavities would have been constructed and tested. Coupling would have been through a waveguide inductive iris into an end wall with a logarithmic decrement technique of Q measurement were considered

most appropriate for the high Q anticipated. An X-band (10 GHxz) frequency choice allows for convenient dimensions of 4.3 cm diameter by 2.8 cm height. However, DARPA/ONR recent recommendation to General Atomics (GA) was to curtail the work on the cavity and concentrate on improving the quality and transport properties of solution condensed films activity.

1.2. CERAMIC SUPERCONDUCTOR FIBER PROCESSING

1.2.1. Fabrication of 20 Microns Diameter Y123 Fibers

In order to improve the flexibility of superconducting fibers for subsequent melt texturing, the diameter of the final heat-treated fiber was targeted to be 20 microns (down from usual 100 microns in the previous reports). To account for the approximately 50-60% shrinkage during heat treatment of the precursor fibers, and assume fiber is to be made by simple extrusion without down-drawing, the opening of the spinneret (die) was set at 50 microns. Due to the precision and smoothness requirements, the die was ordered from Fitech (Italy) (Fig. 1). It is possible to further reduce the diameter of the fiber to 10 microns by stretching (spinning), but the control of processing parameters or handling of the fiber become much more difficult. However, as the fiber diameter is reduced from 100 microns to 20 microns, some processing parameters needs to be modified.

1.2.2 Mixing and Filtering

Mixing of the resin with the binary (polar and non-polar) solvents should be more uniform than previously required since slight inhomogeneity in the resin mass greatly influences the fiber extrusion pressure, or even blocking the opening of the die. It also affects the final fiber mechanical and electrical properties. To improve the uniformity of the resin mass, the resin powder was ground and sieved through a 20 microns sieve so no particles larger than 50 micron could

block the opening of the die. Sometimes, some harder agglomerates still temporarily blocked the spinneret causing breaking in the fiber line. These hard agglomerates could be dissolved by adding solvents at the opening of the die and the fiber line sometime could be resumed. To remove these hard agglomerates (or foreign particles), the die was modified to include an in-line filter (Fig. 2). Copper mesh with opening of 30 and 5 microns has been tried and some success has been made in this front. One problem yet to be solved is the deformation of the fine copper mesh during the filtration of the resin mass. Currently, other filters are being ordered and will be evaluated. Another problem is the hard agglomerates clogging of the die opening increases the extrusion pressure causing O-ring failure.

1.2.3. Leakage in the O-ring

The drastic increase in extrusion pressure caused failure in the O-ring. The O-ring used has a rating only up to maximum pressure of 1500 psi (static application, face seal gland). For current fiber spinning (extrusion), the pressure needed surpasses this limit causing O-ring extrusion and nibbling failures and leaking of the resin mass.
A non-reactive, anti-extrusion backup ring was made out of Teflon to stiffen the O-ring and successfully increase the pressure limit to above 8000 psi (Fig. 2). It has also been observed that the Nitrile-type O-ring integrated with aromatic (non-polar) solvents is more resistance to chemical attack. This situation was corrected by using fluorocarbon type (e.g. Viton^{TM} O-ring).

1.2.4. Transferring the Resin Mass into the Extrusion Die

Previously, the resin powder was first mixed with binary solvent in a closed glass vial equipped with a step-on for solvent addition. The close glass vial prevented the loss of the volatile solvents. After the uniform mixing has been achieved, the resin mass was removed from the vial and pushed into the extrusion die. Rapid solvent evaporation

occurred during this transfer step and resulted in slightly dry surface in the resin mass (imagine pushing a wet chewing gum into a tube). The time needed to transfer the resin mass out of glass vial to the die was approximately 0.5 to 3 min. While it was not always critical for the fabrication of 200 microns precursor fibers, it was more sensitive in the extrusion of 50 microns precursor fibers. The local inhomogeneity reflected in the viscoelastic property of the resin causing instability of the extrusion pressure. The transferring process also introduced large void space in the resin mass. Although void space has not been frequently observed in the previously spun 100-200 microns fiber, it was suspected that it spread out in the interior of the smaller diameter fiber.

To standardize this transferring practice, two transferring adaptors were designed and made of Teflon (Rig. 3). The first adaptor is a seat used to seal the bottom of an open-bottomed glass vial. The use of the glass vial allowed the observation of adding the solvents and mixing the resin mass. After uniform mixing, this seat was quickly removed and the glass vial was directly connected to a side port of a second adaptor (usually this took less than three sec exposure in air). Then the resin mass was gradually pushed through this side port, first using a stick then using a plunger (usually less than 10 sec exposure in air). The pushing by the plunger compacted the resin to a blocky mass and removed some of the large void space during the transferring process. A second plunger, arranged 90° to the side port, then pushed the resin mass down to the extrusion die (no exposure to air). This second plunger also compacted the resin and further removed some of the larger void. The plunger was quickly replaced by a piston used for fiber spinning (exposure time to air 5-15 sec, with limited surface exposure). While this transferring practice is still not perfect and has not solved all the smaller trapped air, it greatly reduces the solvents loss and standardized the transfer process.

1.2.5. Extrusion Pressure

The pressure required for a smooth continuous spinning line has been studied by using an Instron machine. With simple extrusion and no down-drawing, it was found that when the pressure was too high (300-400 lb load, >3600 psi), a melt fracture always occurred resulting in a wavy and kinky fiber. Often, this instability lead to entanglement in the fiber line. Kinks and entanglement still happened quite frequently at slightly lower pressure (>1620 psi). A stable fiber spinning line was maintained at 750 to 1350 psi (80-150 lb load). For initial pressure within this range, stable fiber line sustained for approximately 20-40 min while the pressure gradually decreased. Below 700 psi, no fiber could be extruded. However, pressure needed to maintain the stable fiber line increased as the piston moved down due to the greater friction between the piston and the die wall. Therefore, a constant downward movement of the piston was needed. The downward speed required to maintain this pressure is in the range of 0.002 in./min or below, but this parameter has not been precisely determined.

A compromise had to be made between the extrusion pressure and the output rate of the fiber. Toward the upper pressure limit of the stable fiber line, output rate greater than approximately 1.5 cm/sec can be achieved but the drawback seems to be the fiber line stability. The extruded 50 microns precursor fibers are shown in Fig. 4. Because the optimal extrusion conditions of 50 microns precursor fiber has not been established, the simultaneous down stretching has not been performed. With a simultaneous down-drawing, a final fiber of 10 microns diameter could be made possible.

1.2.6. Removing Waviness of the Fiber (Straighten Process)

It was discovered that for the precursor fibers to have uniform diameter with minimum waviness, a short time annealing at 175-180°C was required to remove this waviness and straightened the fiber. DSC

study indicated a possible irreversible relaxation process occurred in the temperature range of 75-175°C. A reversible thermal effect also occurred below 63°C. Figure. 5(a), shows the DSC trace of precursor fibers in nitrogen atmosphere and Fig. 5(b) is the re-run trace after cooling. The very broad endothermic peak disappeared by the first heating but the larger endothermal peak remained. Even with the 180°C straighten process the waviness occurred if heating rate greater than 0.5°C/min was maintained. The occurrence of the waviness during the high heating rate treatment schedule was thought to be due to overheating. Overheating caused very slight melting in the interior of the fiber and redistributed the liquid phase. This phenomenon will have to be studied further.

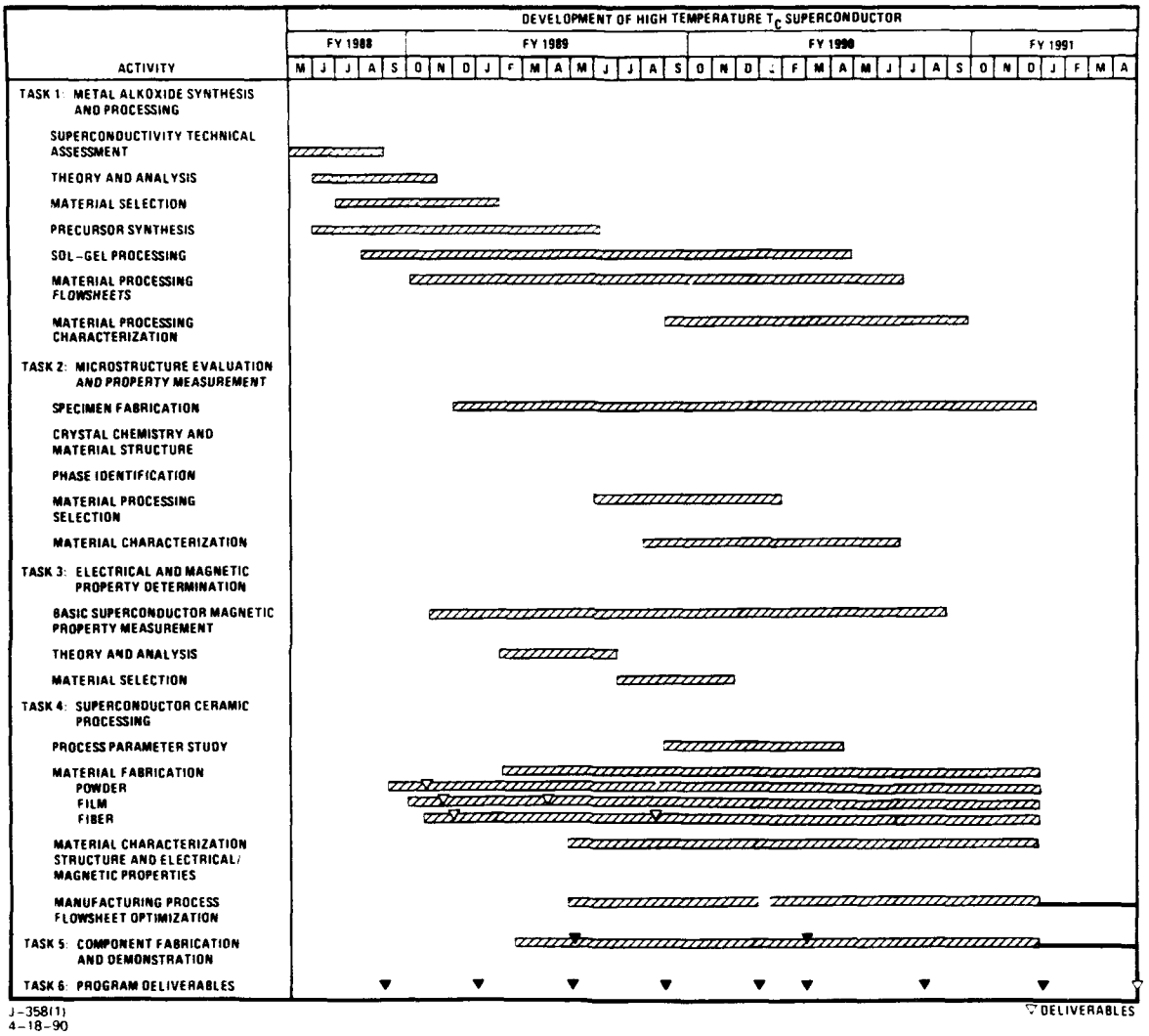
In summary, some modifications in the extrusion die and determination of processing parameters were needed in order to fabricate 20 microns superconducting fiber.

2. PRELIMINARY TESTING OF THE 20 MICRONS SUPERCONDUCTING FIBERS

Currently, straight 18-20 microns diameter superconducting fibers have been obtained after heat treatment. Some fibers exhibit excellent flexibility but others do not. A radius of curvature as small as 2-3 cm has been achieved. However in these flexible straight fibers some microstructure defects, such as small surface cracks and large pores, still exist (Fig. 6). The microstructure defects reduces the tensile strength of the fiber. By removing these defects, fibers will be much stronger. The handling and applying current contacts and silver lead wires to these 20 microns fibers pose some challenge. Some micro-tools are required to routinely handle these fibers for testing.

The electrical properties of these 18-20 microns superconducting fibers has been measured. The T_c are ranging from 92-89K--this depends on heat treatment schedule and resin batches. Occasionally, small tails occurred in the resistance versus temperature curve which lower the T_c (R=0) to about 75-80K. A maximum J_c value of 6300-7500 A/cm^2

(50K, ambient field) has been observed in 18 micron diameter fibers where I_c is 16-19mA. The J_c values varies with heat treatment and somewhat scattered at the present time. This may be due to the microstructure defects described above. Melt-texturing these fiber is in progress.


DEVELOPMENT OF HIGH TEMPERATURE T_C SUPERCONDUCTOR
FY 1988
FY 1989
FY 1990
FY 1991
M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A
ACTIVITY
TASK 1: METAL ALKOXIDE SYNTHESIS AND PROCESSING
SUPERCONDUCTIVITY TECHNICAL ASSESSMENT
THEORY AND ANALYSIS
MATERIAL SELECTION
PRECURSOR SYNTHESIS
SOL-GEL PROCESSING
MATERIAL PROCESSING FLOWSHEETS
MATERIAL PROCESSING CHARACTERIZATION
TASK 2: MICROSTRUCTURE EVALUATION AND PROPERTY MEASUREMENT
SPECIMEN FABRICATION
CRYSTAL CHEMISTRY AND MATERIAL STRUCTURE
PHASE IDENTIFICATION
MATERIAL PROCESSING SELECTION
MATERIAL CHARACTERIZATION
TASK 3: ELECTRICAL AND MAGNETIC PROPERTY DETERMINATION
BASIC SUPERCONDUCTOR MAGNETIC PROPERTY MEASUREMENT
THEORY AND ANALYSIS
MATERIAL SELECTION
TASK 4: SUPERCONDUCTOR CERAMIC PROCESSING
PROCESS PARAMETER STUDY
MATERIAL FABRICATION
POWDER
FILM
FIBER
MATERIAL CHARACTERIZATION STRUCTURE AND ELECTRICAL/ MAGNETIC PROPERTIES
MANUFACTURING PROCESS FLOWSHEET OPTIMIZATION
TASK 5: COMPONENT FABRICATION AND DEMONSTRATION
TASK 6: PROGRAM DELIVERABLES
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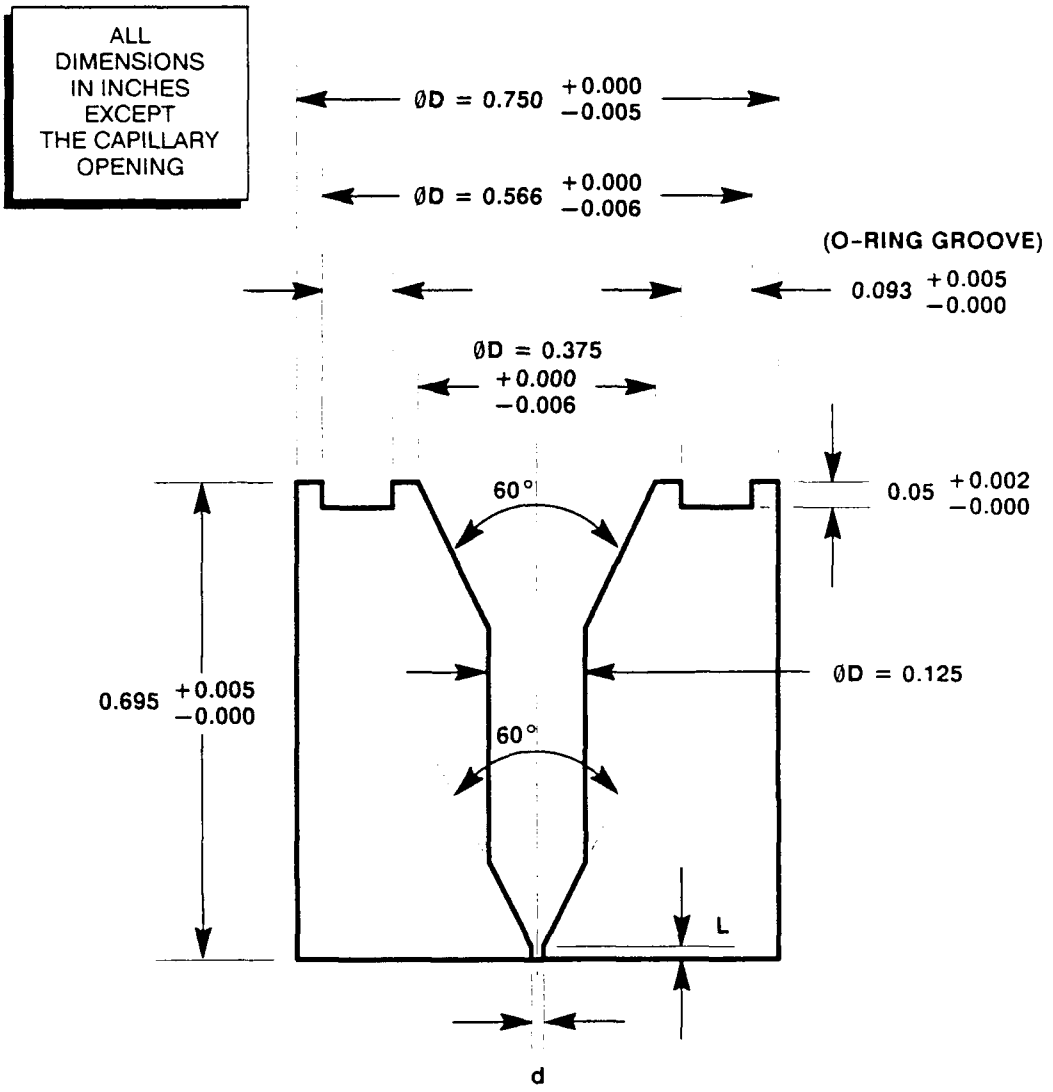
▽ DELIVERABLES

MILESTONE



INSTRUCTIONS

- **ROUND HOLE DIAMETER d = 0.05 mm L/D = 0.07 – 1**
- **TOLERANCE AS STANDARD FOR WET AND DRY SPINNING MIRROR FINISH AT THE CAPILLARY OPENING: 0.02 – 0.05 μ**
- **MATERIAL: STAINLESS STEEL**
- **O-RING FACE GROOVE FOR PARKER NO. 2-013 O-RING**

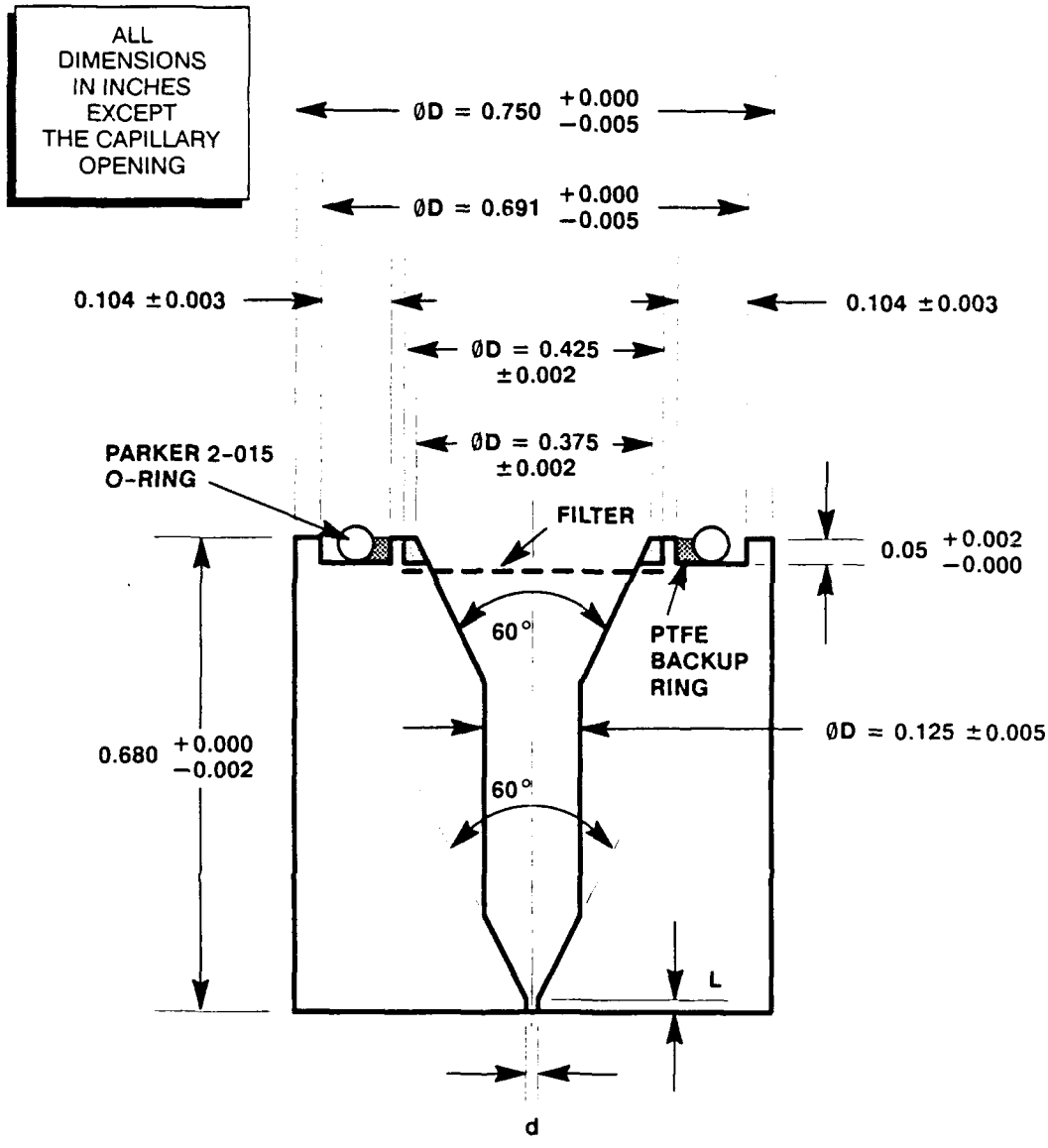
O.D. = 0.566 +0.000 −0.006

DEPTH = 0.050 +0.002 −0.000

WIDTH = 0.093 +0.005 −0.000

K-181(5)(I-01)
8-9-91

Fig.1. The die used for extrusion of 50 μm precursor fiber.



- ROUND HOLE DIAMETER d = 0.05 mm L/D = 0.07 – 1
- TOLERANCE AS STANDARD FOR WET AND DRY SPINNING MIRROR FINISH AT THE CAPILLARY OPENING: 0.02 – 0.05 μ
- MATERIAL: STAINLESS STEEL

(O-RING FACE GROOVE FOR PARKER NO. 2-015 OUTWARD PRESSURE; LIQUID)

- O.D. = 0.566 +0.000 −0.006

  DEPTH = 0.050 +0.002 −0.000

  WIDTH = 0.093 +0.005 −0.000

K-181(4)(I-01)
8-9-91

Fig. 2. The modified die for filtering agglomerated or foreign particles and increasing O-ring pressure limit from 1500 psi to 8000 psi.

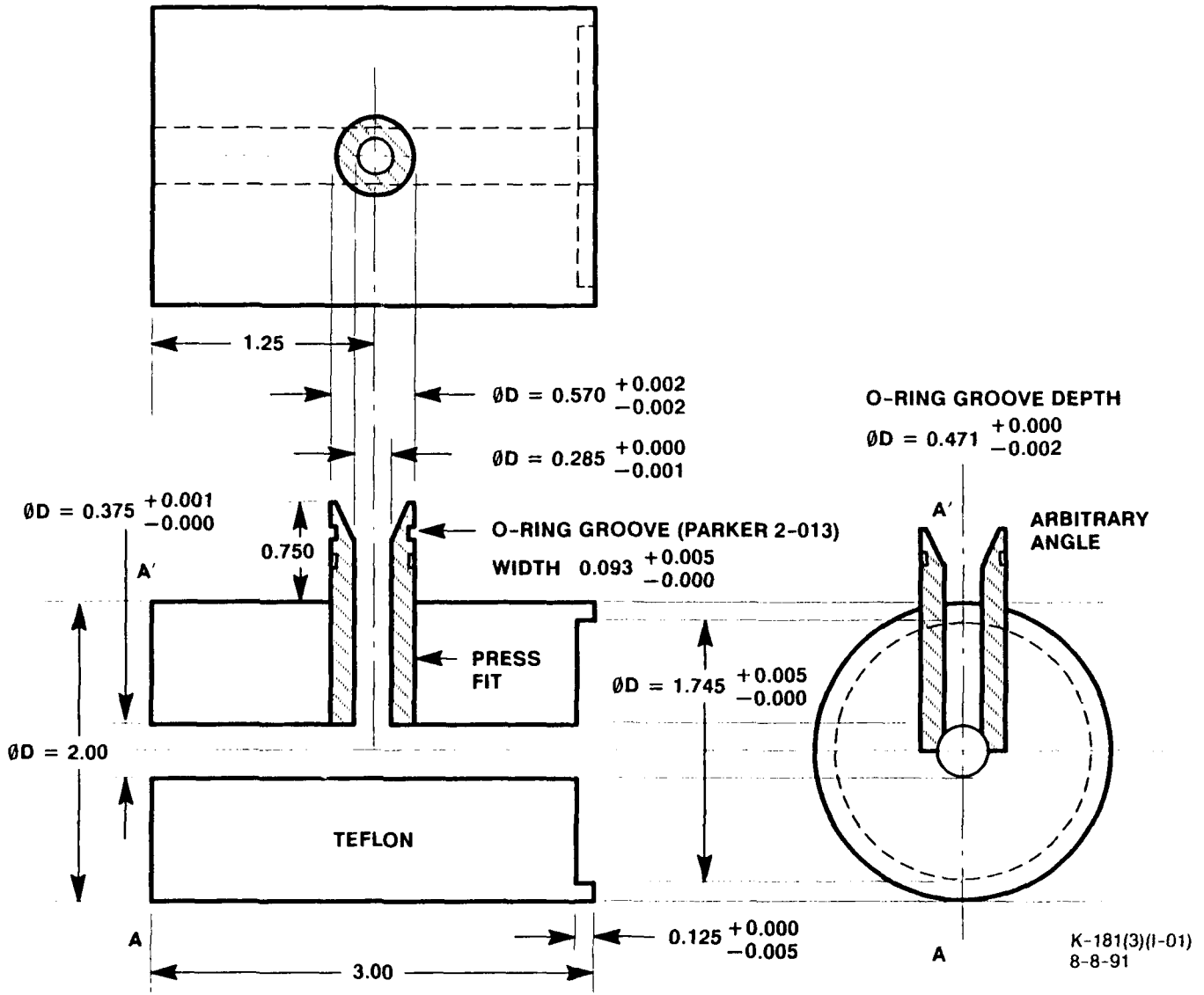


Fig. 3. The adaptor for transferring resin mass.

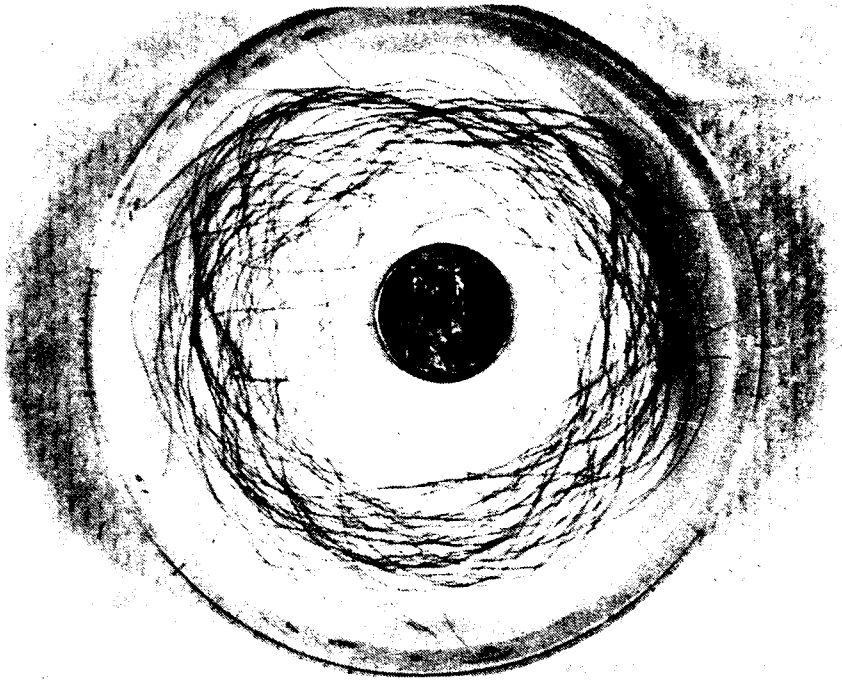


Fig. 4. The extruded 50 micron precursor fibers.

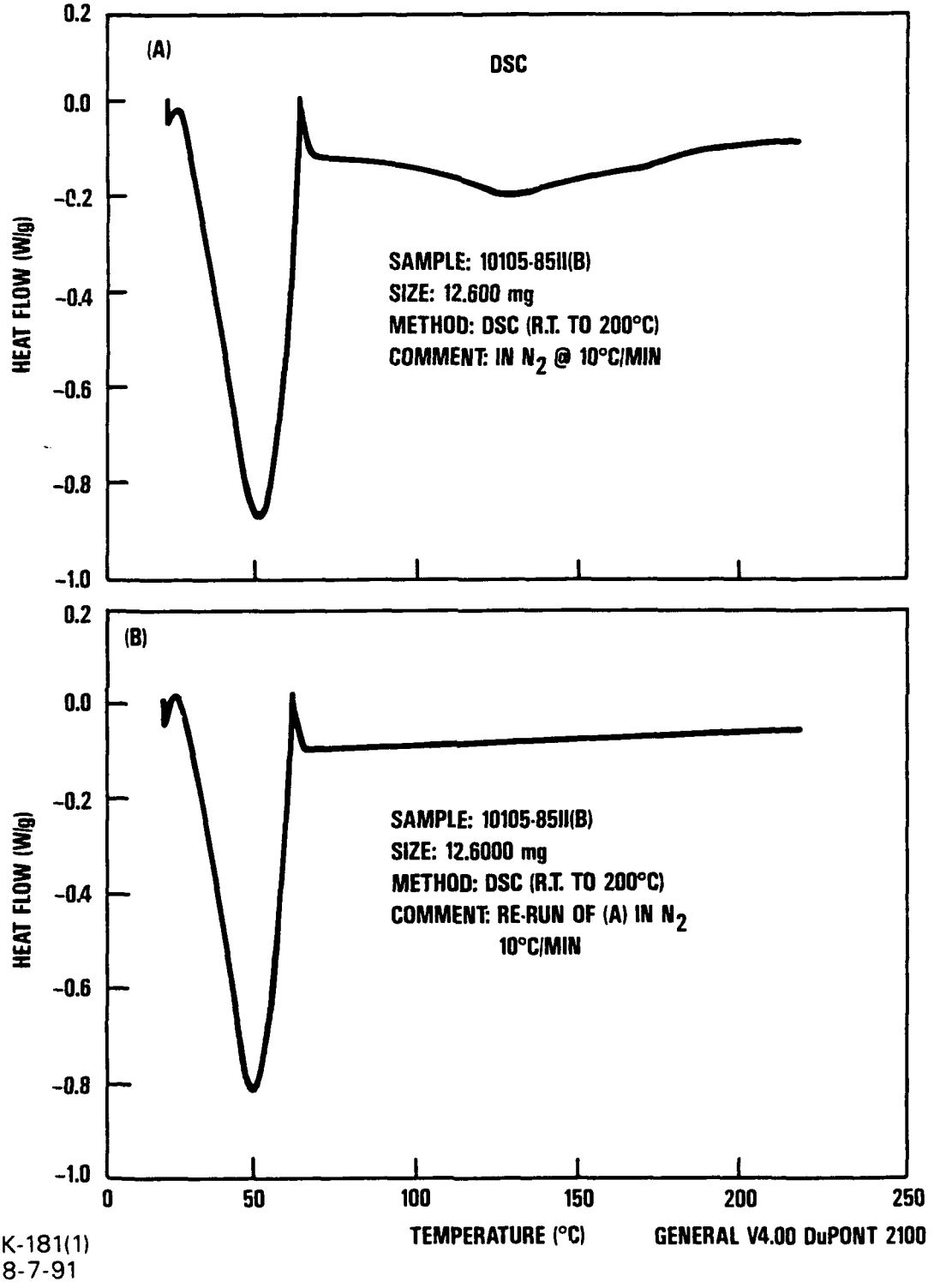


Fig. 5. DSC curves of precursor fibers showing an irreversible endothermal peak from 75-175°C and a reversible peak at 50°C; (a) first run (b) re-run of the same sample.

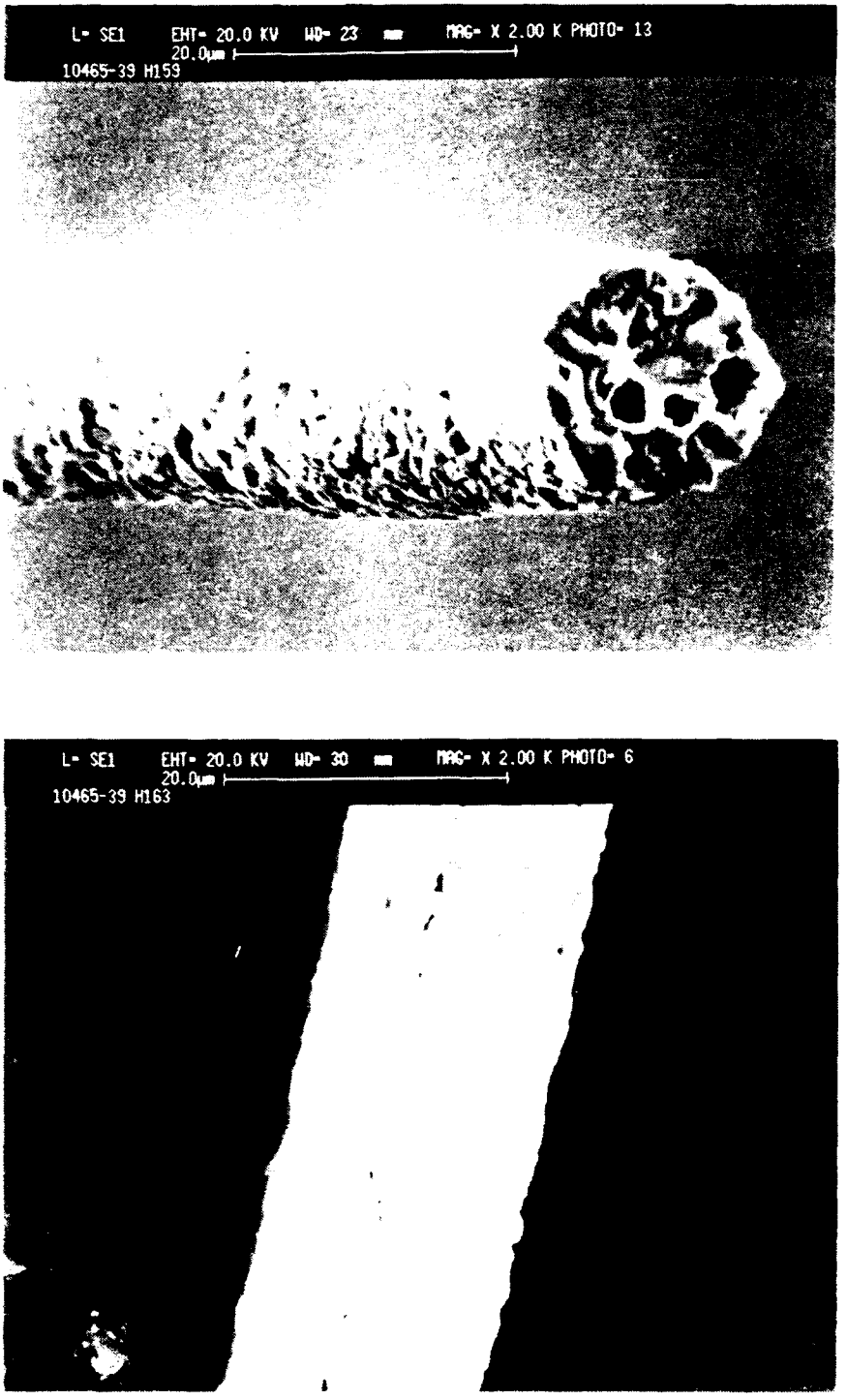


Fig. 6. Some microstructural defects observed in the 20 μm superconducting fibers; (a) porosity and (b) surface crack.